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Pseudopotential Calculations of Electronic Charge Densities in Seven Semiconductors*

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Electronic charge densities are calculated as a function of position in the unit cell for seven diamond and zinc-blende semiconductors using wave functions derived from pseudopotential band-structure calculations. Detailed plots of the charge density are presented in the $(1\bar{1}0)$ plane for each valence band of Ge, GaAs, and ZnSe and for the sum of the valence bands of Ge, GaAs, ZnSe, α-Sn, InSb, CdTe, and Si. Trends in bonding and ionicity are discussed in detail. The covalent-bonding charge is also calculated for these crystals and is plotted against the ionicity scales of Phillips and Van Vechten and of Pauling. It is shown that an extrapolation to zero covalent-bonding charge yields a critical value of the ionicity which separates fourfold-coordinated and sixfold-coordinated diatomic crystals. This value is in agreement with the empirical value obtained by Phillips and Van Vechten.

INTRODUCTION

We present[1] here calculations of the electronic charge density for Ge, GaAs, ZnSe, α-Sn, InSb, CdTe, and Si (each of which has either the diamond or zinc-blende crystal structure). The results of the charge-density calculations are used to analyze the bonding properties of these crystals. Studies of bonding properties have recently received[2-7] a great deal of attention from solid-state physicists, and we hope the detailed calculations presented here will both aid in clarifying the appropriateness of the current models used and will result in calculations of properties of interest to solid-state chemists and physicists.

The charge density was calculated using wave functions obtained from band-structure calculations for these materials. The band structures were computed using the pseudopotential method.[8] Since the wave functions can be obtained for each valence and conduction band individually, the charge density was calculated band by band for each material. Although the variation of the charge distribution with band index or with changes in elements may not yield accurate quantitative results, observation of trends occurring in a series of crystals can yield a physical picture for why crystals behave as they do. For some of the crystals, the charge density for the first conduction band (assuming it were filled with carriers) is given showing the free-electron nature of this band.

Finally, to illustrate the bonding nature of these solids the charge-density distributions are used to compute covalent-bonding charges, which in turn are used to compute the critical ionicity f_c which separates fourfold-coordinated and sixfold-coordinated diatomic crystals.

CALCULATIONS

The electronic wave functions used in the charge-density calculations were obtained from the band-structure calculation based on the pseudopotential method.[8] Briefly, the method involves solving a secular equation for the pseudopotential Hamiltonian which has the form

$$H = -(\hbar^2/2m)\nabla^2 + V(\vec{r}) \quad . \tag{1}$$

To take advantage of the crystal symmetry, the weak crystalline pseudopotential $V(\vec{r})$ is expanded in the reciprocal lattice

$$V(\vec{r}) = \sum_{\vec{G}} V(|\vec{G}|)e^{-i\vec{G}\cdot\vec{r}} , \tag{2}$$

where $\vec{G}$ is a reciprocal-lattice vector. For two atoms per cell (diamond and zinc-blende structures) it is convenient to express $V(\vec{G})$ in terms of atomic pseudopotential form factors $V_1(\vec{G})$ and $V_2(\vec{G})$ in the following way:

$$V(\vec{G}) = V^S(\vec{G})\cos\vec{G}\cdot\vec{\tau} + i\,V^A(\vec{G})\sin\vec{G}\cdot\vec{\tau} \ , \tag{3}$$

where $V^S(\vec{G})$ and $V^A(\vec{G})$ are the symmetric and antisymmetric parts of the potential, the basis vector $\vec{\tau} = (a/8)(1, 1, 1)$, and a is the lattice constant. In terms of atomic potentials

$$V^S(\vec{G}) = \tfrac{1}{2}[V_1(\vec{G}) + V_2(\vec{G})] , \tag{4}$$

$$V^A(\vec{G}) = \tfrac{1}{2}[V_1(\vec{G}) - V_2(\vec{G})] , \tag{5}$$

$$V_{\substack{1\\2}}(\vec{G}) = (2/\Omega)\int V_{\substack{1\\2}}(\vec{r})e^{+i\vec{G}\cdot\vec{r}}\,d^3r \ , \tag{6}$$

where Ω is the volume of the unit cell. In these calculations, only the six pseudopotential form factors $V^S(\sqrt{3})$, $V^S(\sqrt{8})$, $V^S(\sqrt{11})$, $V^A(\sqrt{3})$, $V^A(2)$, and $V^A(\sqrt{11})$ are allowed to be nonzero; i.e., zero values are taken for $G^2 \geq 12$ and for the cases where the structure factors $\cos\vec{G}\cdot\vec{\tau}$ and $\sin\vec{G}\cdot\vec{\tau}$ are zero. For the diamond structure, $V^S(\vec{G}) = V_1(\vec{G}) = V_2(\vec{G})$, and $V^A(\vec{G}) = 0$.

Once the pseudopotential form factors are chosen,[9] the Hamiltonian [in Eq. (1)] can be solved for the energy eigenvalues and wave functions $\psi_{n,\vec{k}}(\vec{r})$(band n, state $\vec{k}$) at many points in the Brillouin zone. The resulting wave functions can then be used to compute the charge density by noting that the probability of finding an electron in a certain spatial region of volume $d\Omega$ is given by $|\psi_{n,\vec{k}}(r)|^2 d\Omega$, where n is the index of the energy eigenvalue associated with the state $\vec{k}$. When many different electronic states $\vec{k}$ are considered, it becomes meaningful to speak of a charge distribution for the electrons. In particular, the charge density for each valence band may be written

$$\rho_n(\vec{r}) = \sum_{\vec{k}} e|\psi_{n,\vec{k}}(\vec{r})|^2 , \qquad (7)$$

where the summation is over all states in the Brillouin zone.[10]

To obtain adequate convergence in calculating $|\psi_{n,k}|^2$, it is necessary to represent each $\psi_{n,k}$ in an expansion of about 90 plane waves.[11] The wave functions are evaluated on a grid of 3360 points in the Brillouin zone. The coordinates of the grid points are given by $\frac{1}{16}(2s+1,\ 2m+1,\ 2n+1)$ units of $(2\pi/a)$, where s, m, and n are integers.

To illustrate the results and show the bonding characteristics in detail, the charge density $\rho_n(\vec{r})$ is evaluated at over 1500 points in a plane which intersects both atoms in the primitive cell. The plane chosed is a $(1\bar{1}0)$ plane and a diagram of this plane and its orientation with respect to the surrounding atoms is shown in Fig. 1. In the following discussion the values of $\rho_n(\vec{r})$ will be shown in contour and dot-density plots in this plane. The density is plotted in units of (e/Ω), where Ω is the volume of the primitive cell, $\Omega = a^3/4$.

CHARGE-DENSITY RESULTS

Si, Ge, and Sn occur in the diamond crystal structure while GaAs, ZnSe, InSb, and CdTe occur in the zinc-blende crystal structure. It is important to recognize that for both classes of crystals, each atom has four nearest neighbors, arranged tetrahedrally. A $(1\bar{1}0)$ plane intersecting an atom also intersects two of its nearest neighbors (see Fig. 1). There are a total of eight valence electrons per primitive cell and two valence electrons per energy band.

The results of these calculations are shown in both detailed contour maps and dot-density plots for the four valence energy bands and one conduction energy band of Ge, GaAs, and ZnSe and for the sum of the valence bands of Ge, GaAs, ZnSe, Sn, InSb, CdTe, and Si (Figs. 2–23). The contour and dot-density plots are striking and can be used to describe selected physical properties of crystals to a more general audience. For example, tetrahedral covalent bonding can be seen clearly in germanium and ionic trends in bonding are immediately discerned by comparing Ge, GaAs, and ZnSe. The tetrahedral structure is caused by the structure factors in the Hamiltonian from Eq. (3).

First we shall examine the charge-density distribution for each of the valence bands of Ge, GaAs, and ZnSe. The elements in these semiconductors are all in the fourth row of the Periodic Table. Their lattice constants and ion cores are practically identical. This choice allows us to examine ionic trends in crystals that are otherwise expected to have nearly the same properties.

Ge

In band 1 (the valence band of lowest energy), most of the electronic charge is distributed around the atoms with a slight buildup between the atoms (Fig. 2). Band 2 is almost identical to band 1, with only slightly more buildup between the atoms (Fig. 3). A significant change occurs in band 3, where there is practically no charge at the atomic sites and a sharp increase in charge density as the point halfway between atoms is approached (Fig. 4). This concentration of charge between nearest Ge atoms (the covalent bond) is the sharing of electrons caused by quantum-mechanical effects. The concentration of bonding charge is

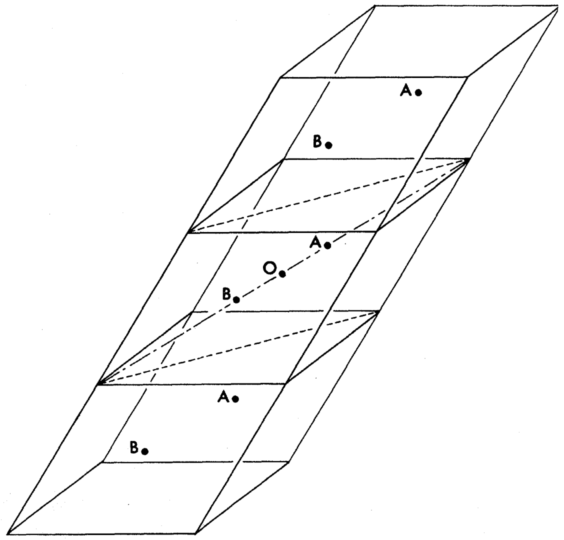

FIG. 1. Location of atoms in the primitive cells. A section of $(1\bar{1}0)$ plane is shown bounded by dashed lines. This bounded plane passes through both atoms A and B. The extended plane passes through all of the atoms shown in the diagram. Each atom has four nearest neighbors bonded tetrahedrally.

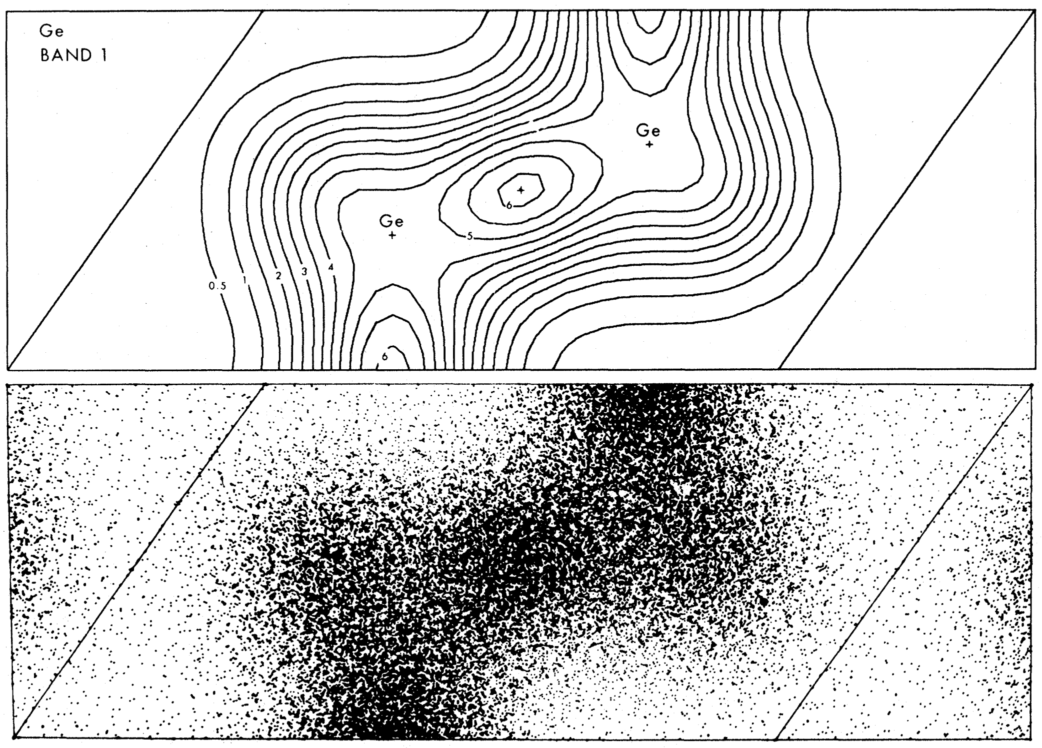

FIG. 2. Valence electron density contour map (in units of e per primitive cell) and dot-density plot for band 1 of Ge in the $(1\bar{1}0)$ plane. The radii of the cores for Ge is 0.20 of the Ge-Ge distance. This radius is that of a sphere containing 80% of the outermost shell of core electrons.

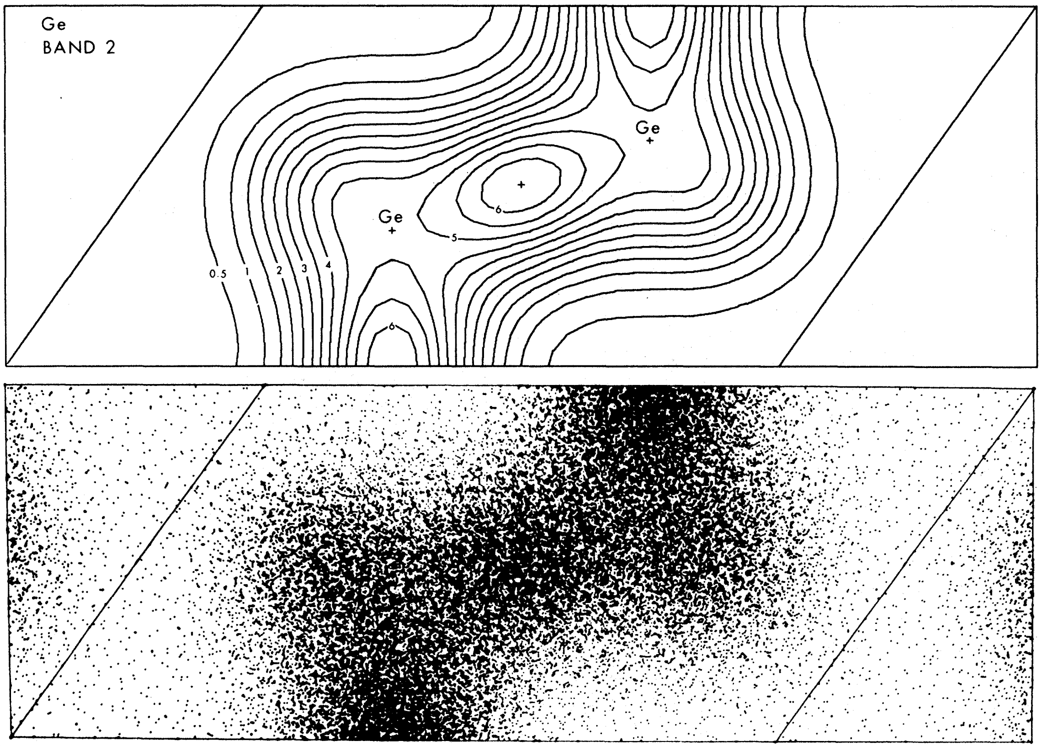

FIG. 3. Ge charge density—band 2.

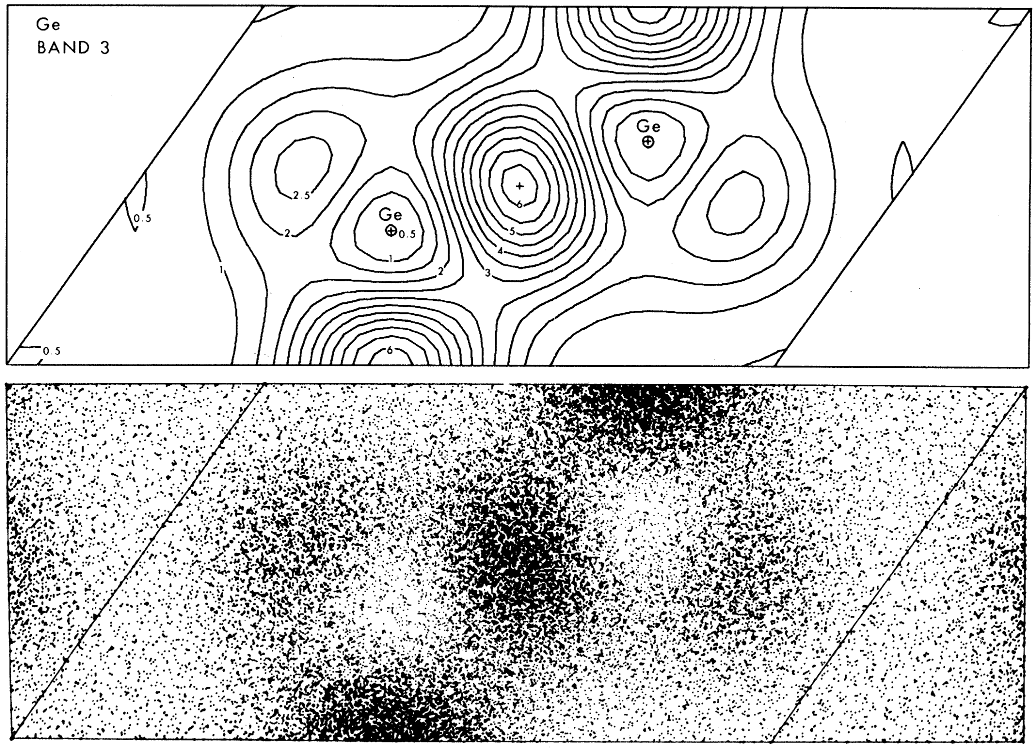

FIG. 4. Ge charge density—band 3.

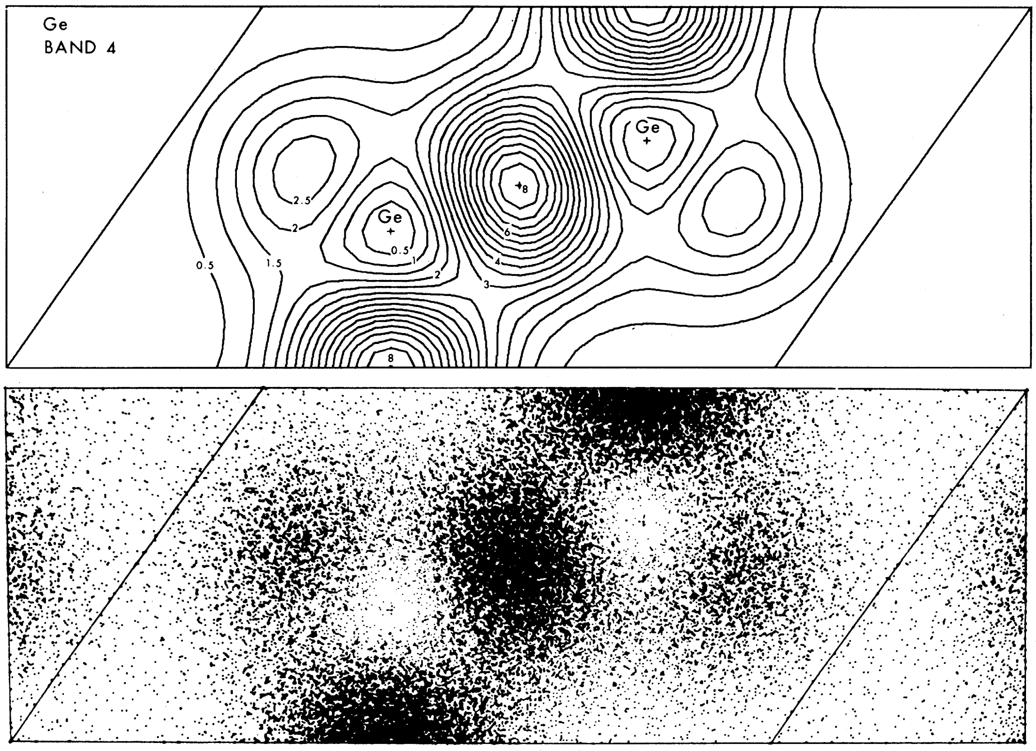

FIG. 5. Ge charge density—band 4.

most pronounced in band 4 (Fig. 5).

The charge distribution is "*s*-like" in bands 1 and 2 (charge concentrated near atoms) and "*p*-like" in bands 3 and 4 (charge concentrated in the covalent bonds). The trend in going from band 1 to band 4 is the increase of charge in the covalent bonds. Of course, this is consistent with the idea that those electrons less tightly bound to the Ge atoms are more likely to be engaged in covalent bonding. Covalent bonding is seen to be an important factor in the total valence charge distribution (Fig. 6).

It is interesting to consider what the charge distribution would be if there were enough electrons to fill band 5, the first conduction band (Fig. 7). The result for Ge is that the fifth band has a nearly constant charge-density distribution. An exactly constant spatial charge distribution would signify a free-electron distribution, so the results for band 5 are consistent with electrons which are essentially free electrons.

GaAs

In band 1 a significant portion of the charge density is in the neighborhood of the As ion (Fig. 8). The reason for this becomes clear if one considers a hypothetical crystal of GaAs with the electrons removed. If enough electrons are put into the crystal to fill the first band, the electrons will be attracted more to the As^{+5} ion than to the Ga^{+3} ion, causing the As ion now to appear as As^{+3}. This distribution clearly has *s*-like character. In band 2 the charge distribution shows much more covalent character and is now displaced toward the Ga ion slightly (Fig. 9). This distribution appears to be a mixture of *s* and *p* character, i.e., there is charge at both the ion sites and the bonding sites. In bands 3 and 4 the covalent charge buildup is even greater and the charge distribution favors the As ion (Figs. 10 and 11). This is clearly *p*-like bonding, since there is a negligible amount of charge density at the ion sites and a high charge density at the bonding sites. The sum of the valence bands shows the covalent-bonding charges, displaced toward the As atom (Fig. 12). Band 5 (Fig. 13) is free-electron-like, although it is not as pronounced as band 5 of Ge. For both Ge and GaAs it is clear that band 5 shows no evidence of covalent-bonding charge.

ZnSe

The Zn and Se ions have a charge of +2 and +6, respectively. Consequently, the charge distribution in ZnSe continues the trend we have seen in going from Ge to GaAs. In band 1 almost all of the charge density is concentrated about the Se ion (Fig. 14). We argue in the same manner as for GaAs, except that now Se has a greater positive charge. The distribution clearly has *s*-like character with respect to Se. Bands 2, 3, and 4 (Figs. 15-17) are all *p*-like in character, and the trend is to increase the charge density in the bonding regions. These bonding regions are much closer to the Se than to the Zn. For the sum of the valence bands (Fig. 18), there is but little covalent-bonding charge noticeable above the background. The total charge density is noticeably concentrated about the Se atom. The trend in Ge to GaAs to ZnSe is toward a more ionic distribution of charge and less covalent bonding. There is also a trend for the first band to be more *s*-like about the anion and the upper bands to become more *p*-like.

Band 5 of ZnSe is somewhat different than band 5 of Ge or GaAs. There is a pronounced concentration of charge in the lower left portion of Fig. 19. This is precisely in the opposite direction to the normal bonding site. This is similar to the so-called antibonding site predicted for excited states by molecular-orbital theory.[12] There is also a peak in the charge density at the site of the Se ion, but there is no concentration of charge at the covalent-bonding sites.

Sn, InSb, and CdTe

The elements in this series of semiconductors are all in the fifth row of the Periodic Table, and in addition, their lattice constants and ion cores are practically identical. Because of their relative positions in the Periodic Table, the physical and chemical properties of Sn, InSb, and CdTe are expected to closely resemble those of Ge, GaAs, and ZnSe, respectively. However, since spin-orbit effects have been neglected in our calculations and since spin-orbit effects are relatively large in the Sn series of crystals, the results for this series are not expected to be as good as for the series Ge, GaAs, and ZnSe. A comparison of the charge distributions for the sum of the valence bands of Ge and Sn (Figs. 6 and 20), of GaAs and InSb (Figs. 12 and 21), and of ZnSe and CdTe (Figs. 18 and 22) shows that the differences between pairs is remarkably small. Since the trends are so similar, the plots for individual bands have been deleted for these three crystals. However, all the discussion for the series Ge, GaAs, and ZnSe is also appropriate for this series of crystals.

Si

The charge-density distribution for the sum of the valence bands of Si (Fig. 23) is included for completeness. The discussion for Ge is also appropriate for Si.

APPLICATION TO BONDING

For the two series of crystals (Ge, GaAs, ZnSe

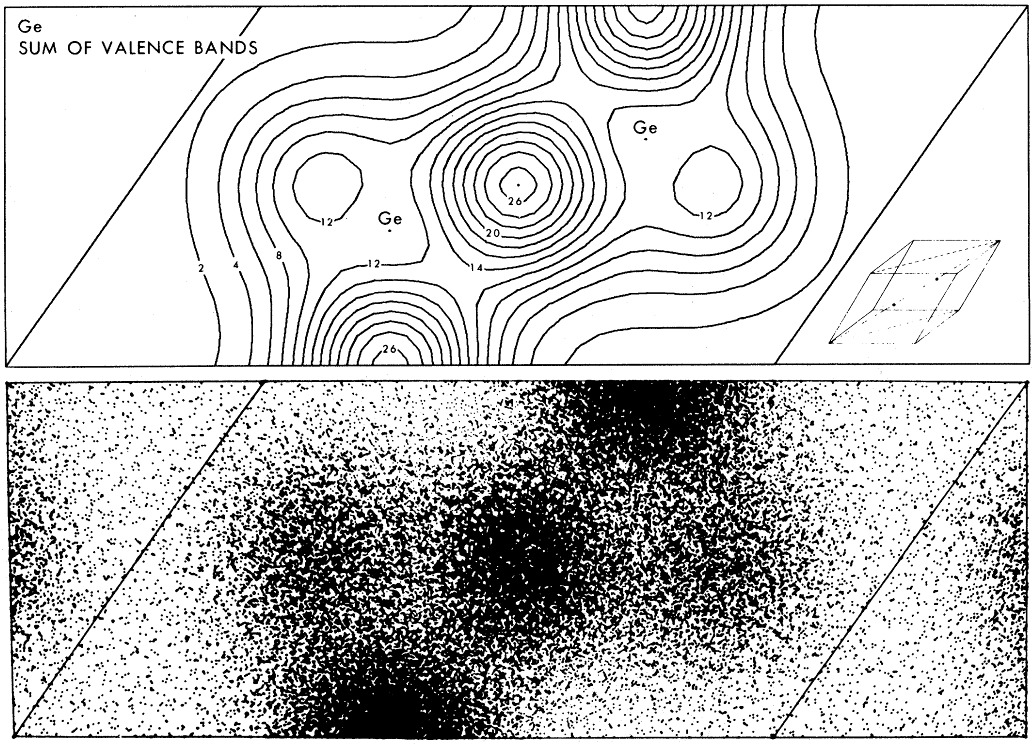

FIG. 6. Ge charge density—sum of valence bands 1–4.

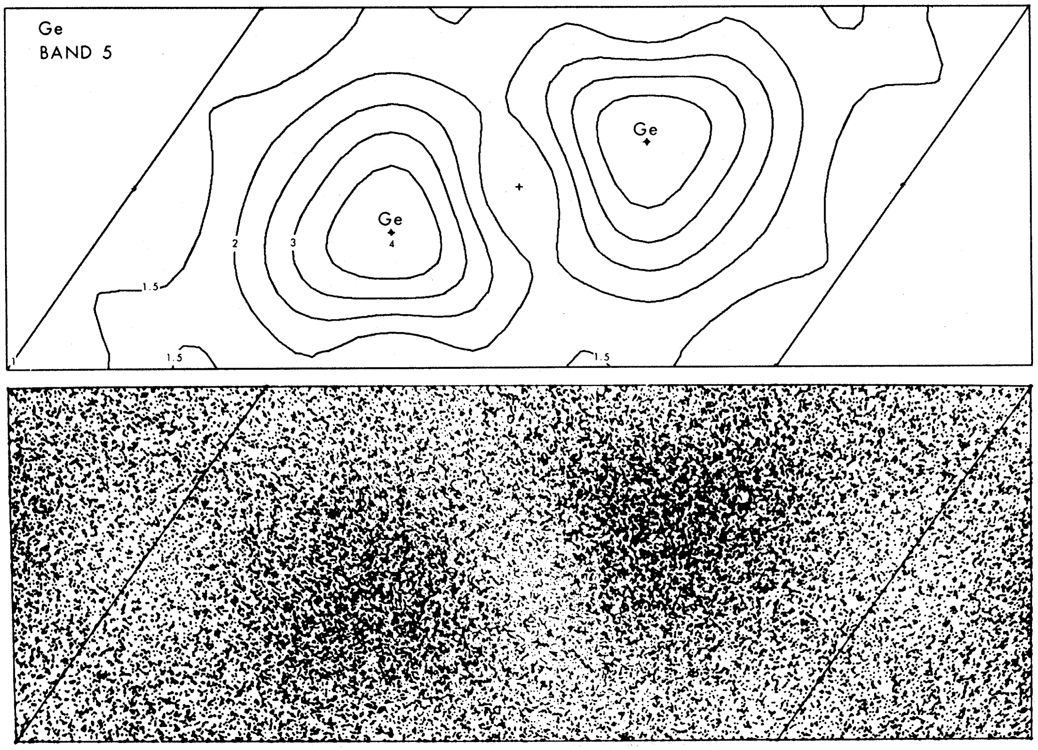

FIG. 7. Hypothetical charge density for the first conduction band of Ge.

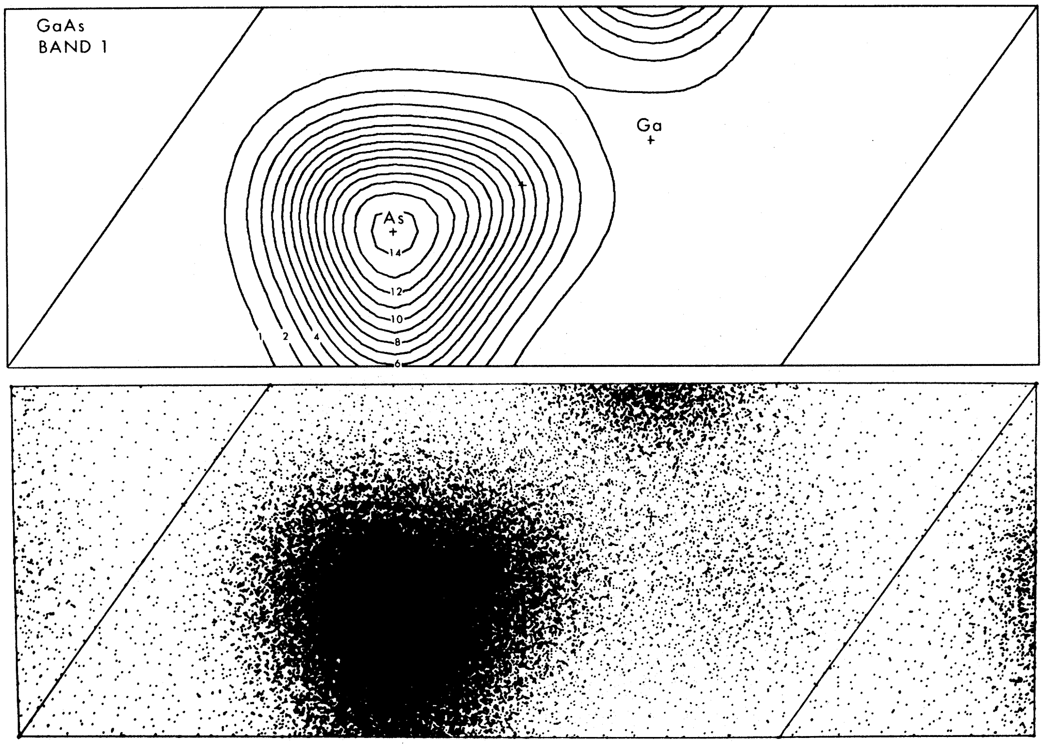

FIG. 8. GaAs charge density—band 1. The core radii for Ga and As are 0.23 and 0.18 of the Ga-As distance. The radii are those of spheres containing 80% of the outermost shell of core electrons.

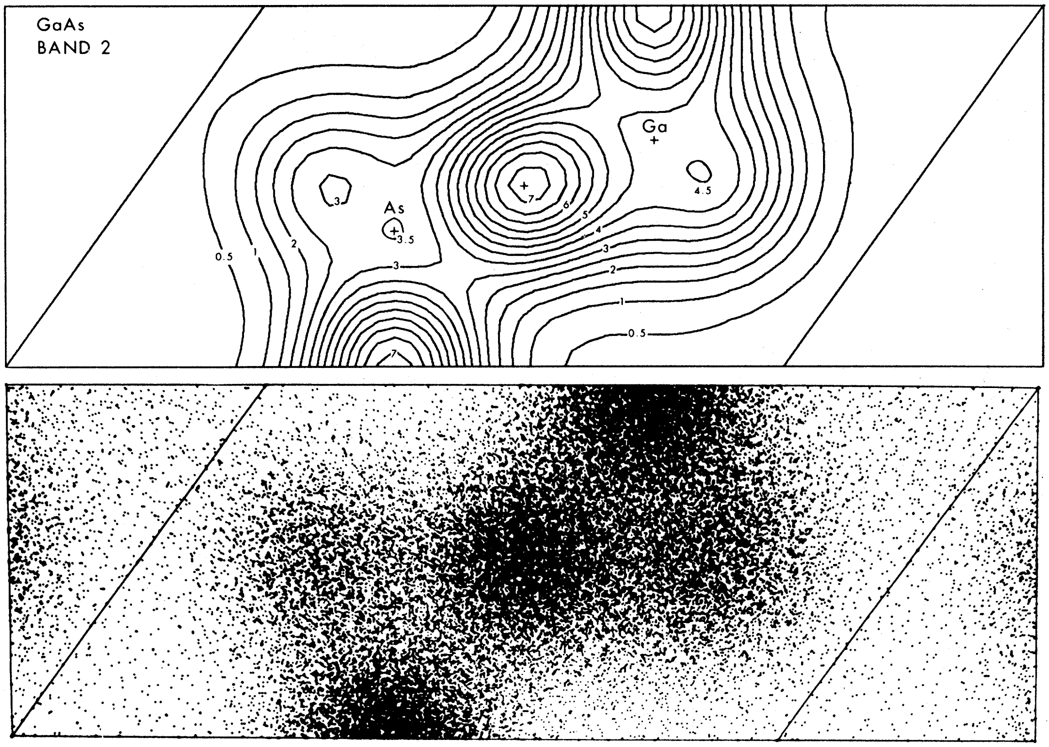

FIG. 9. GaAs charge density—band 2.

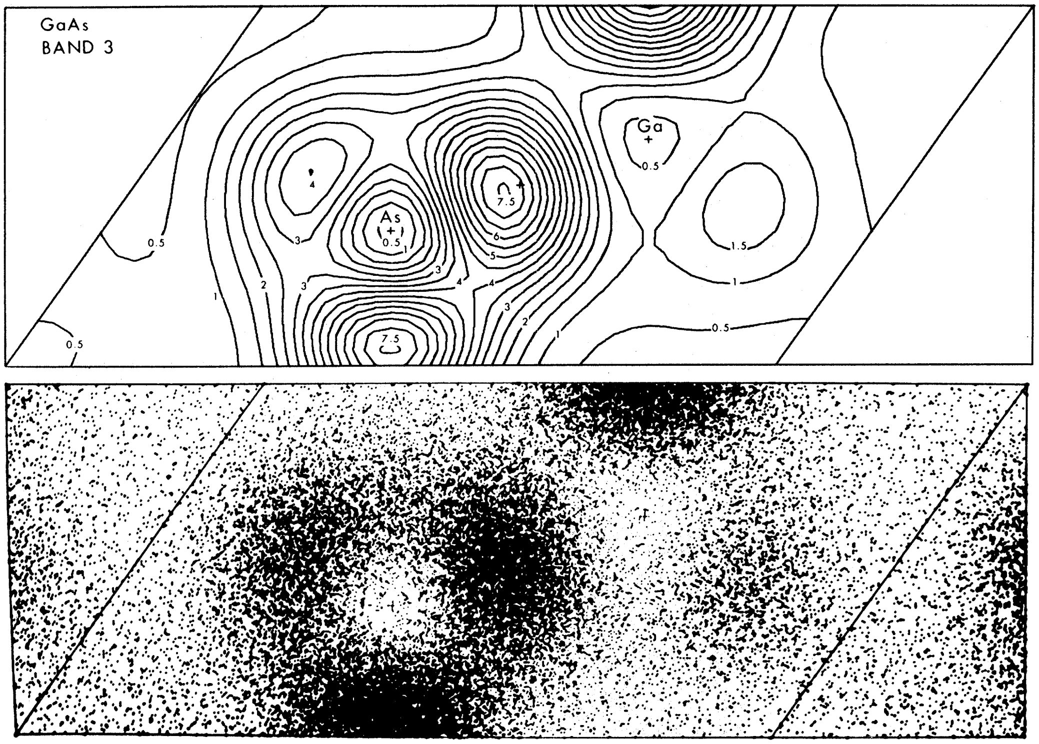

FIG. 10. GaAs charge density—band 3.

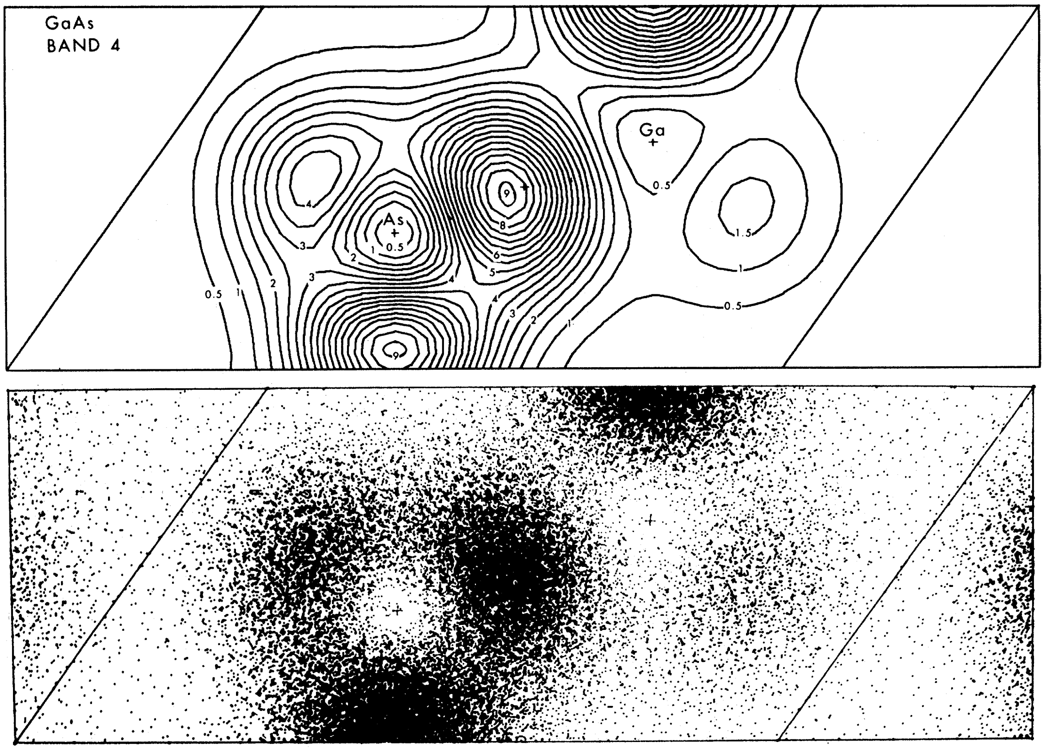

FIG. 11. GaAs charge density—band 4.

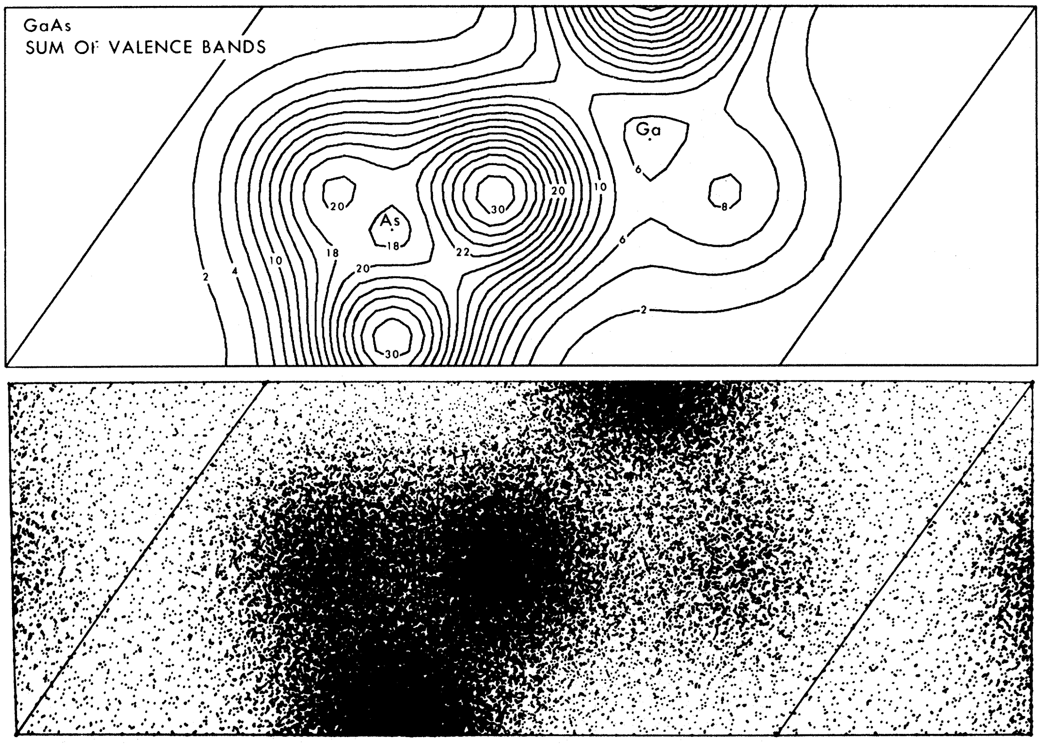

FIG. 12. GaAs charge density—sum of valence bands 1–4.

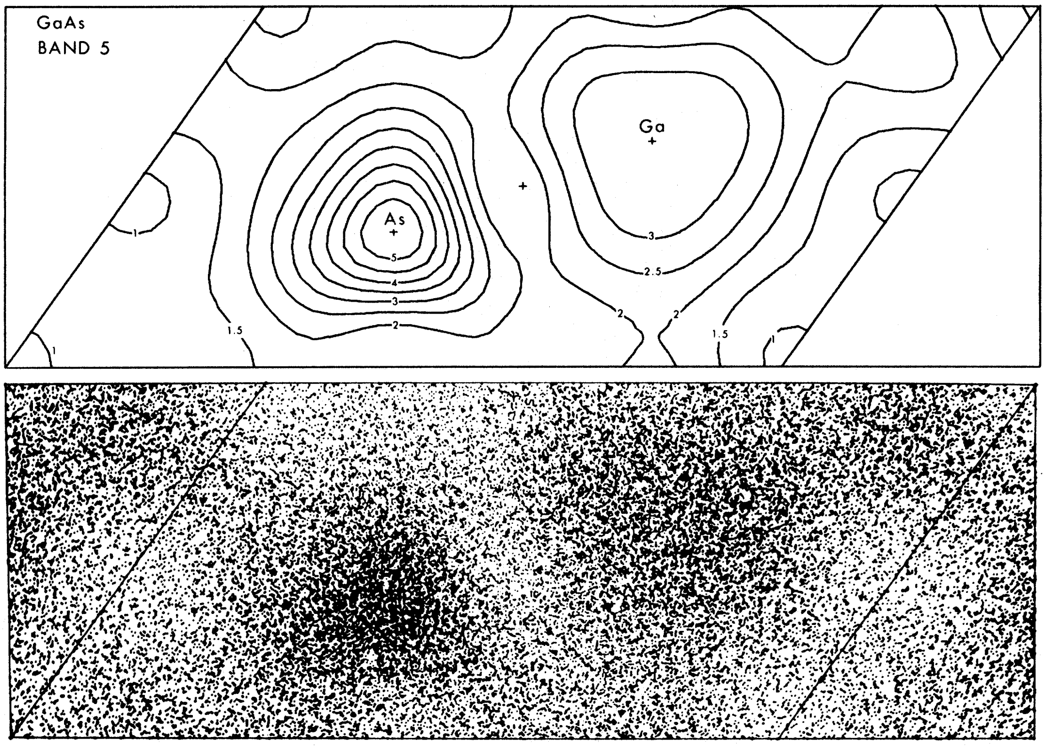

FIG. 13. Hypothetical charge density for the first conduction band of GaAs.

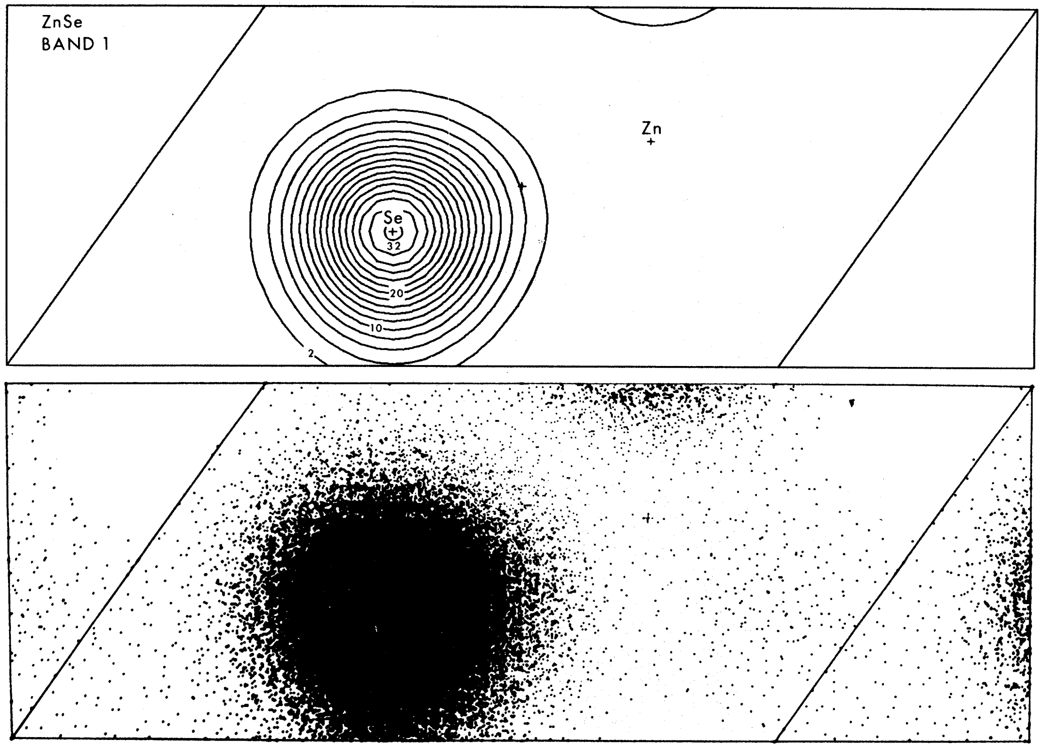

FIG. 14. ZnSe charge density—band 1. The core radii for Zn and Se are 0.24 and 0.15 of the Zn-Se distance. The radii are those of spheres containing 80% of the outermost shell of core electrons.

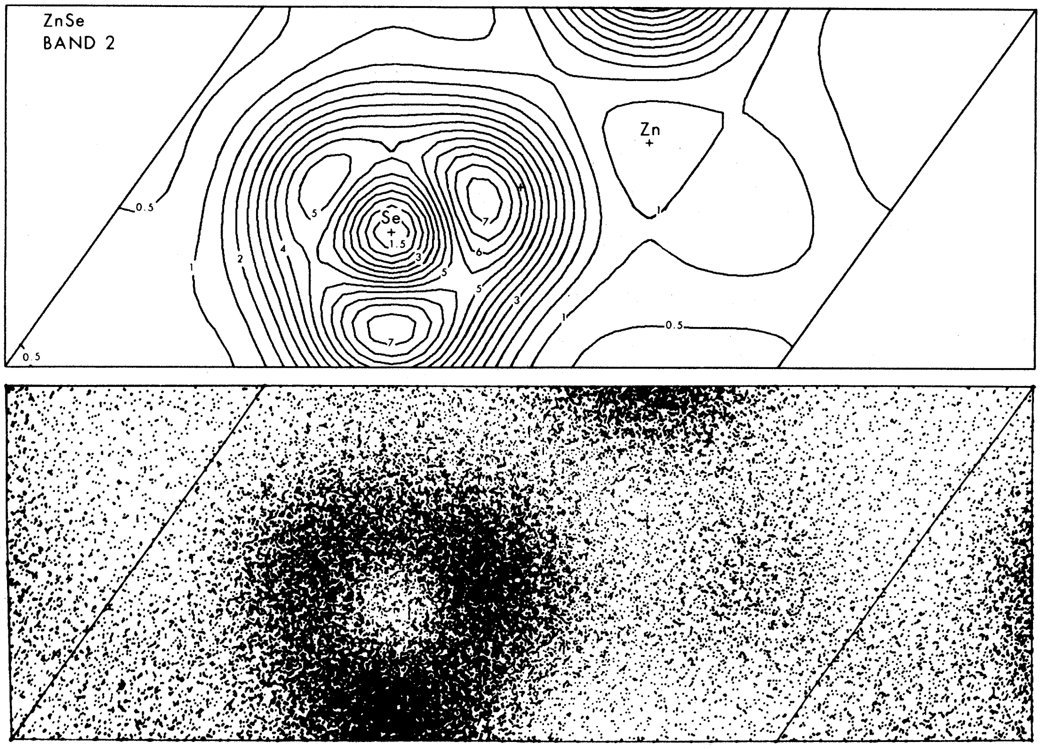

FIG. 15. ZnSe charge density—band 2.

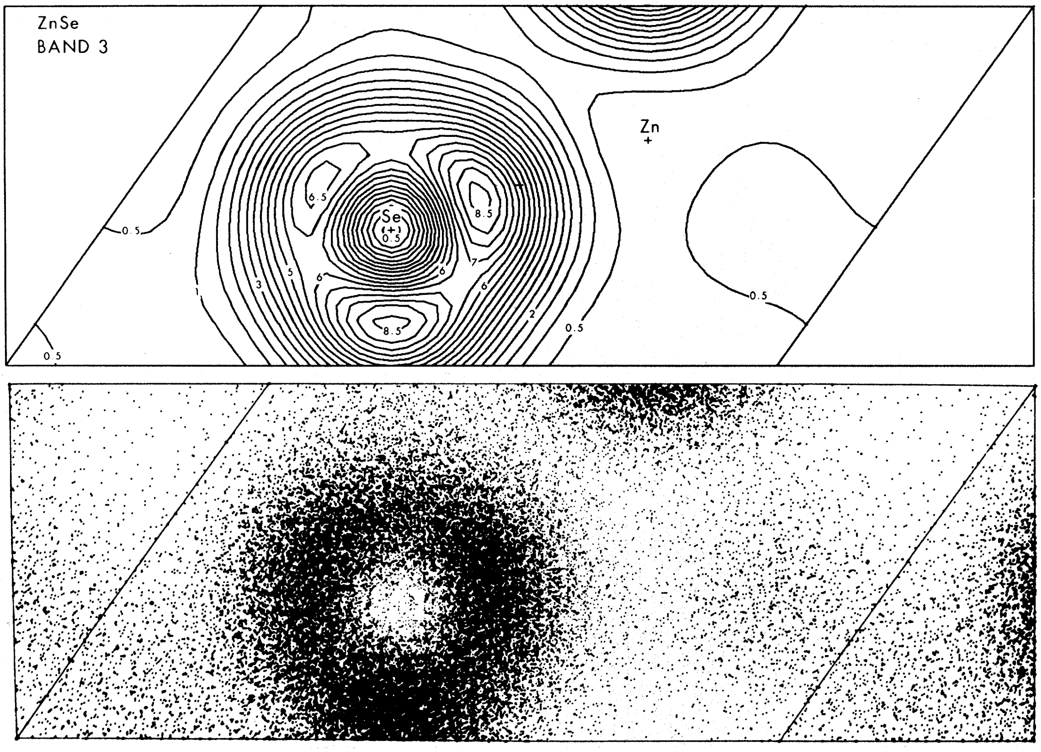

FIG. 16. ZnSe charge density—band 3.

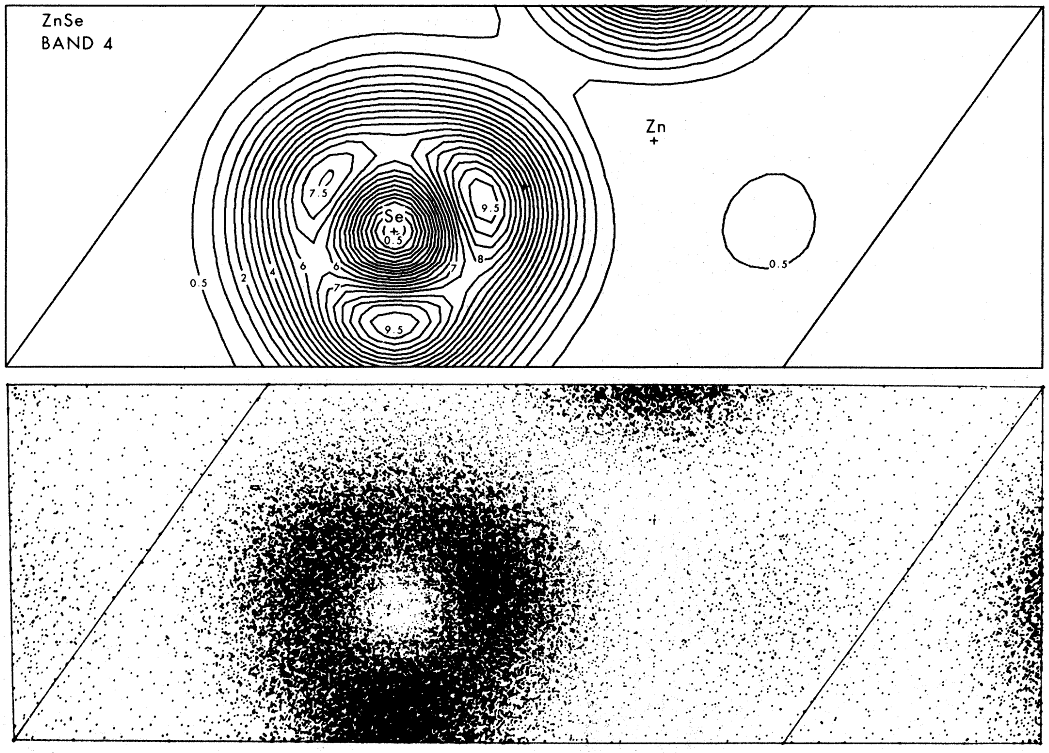

FIG. 17. ZnSe charge density—band 4.

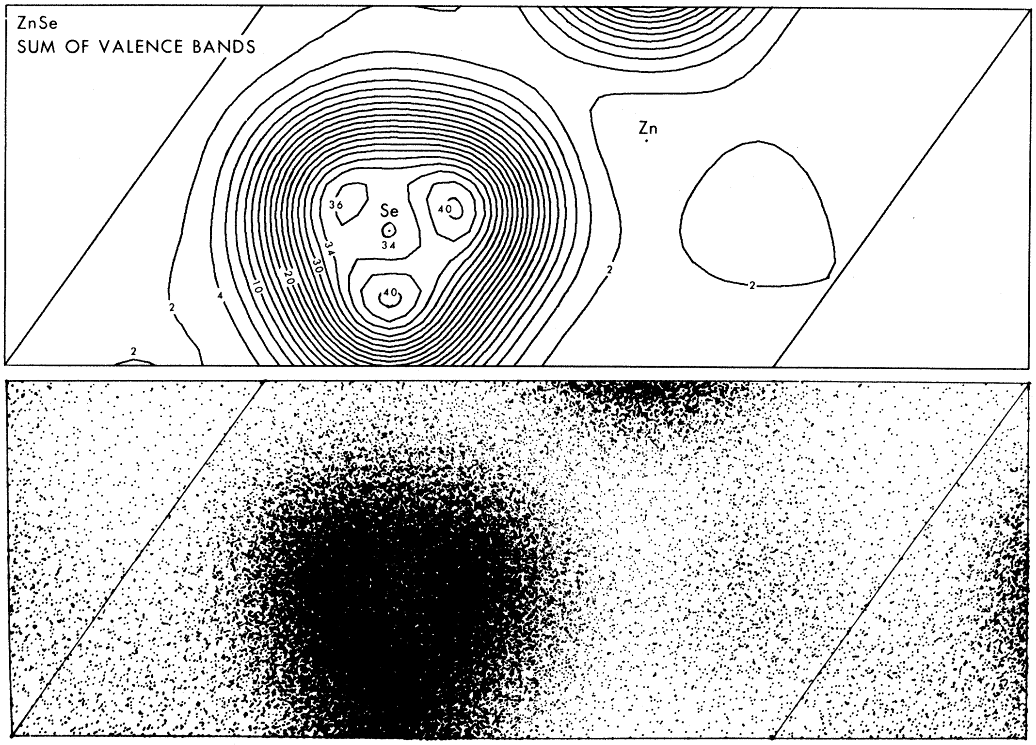

FIG. 18. ZnSe charge density—sum of valence bands 1–4.

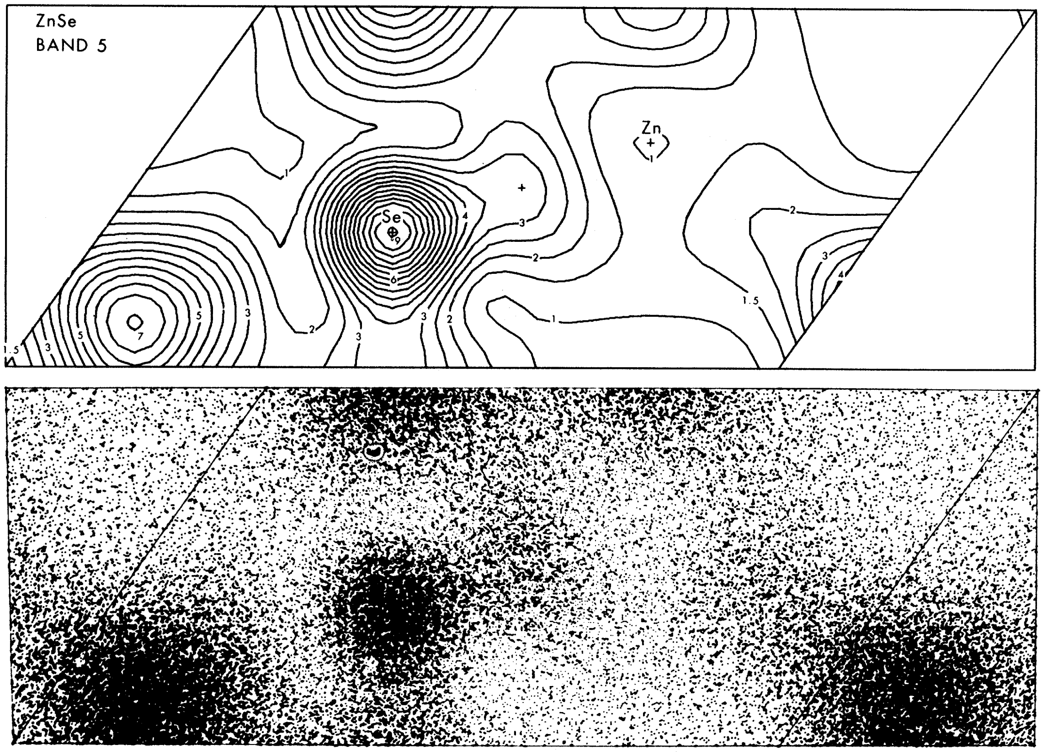

FIG. 19. Hypothetical charge density for the first conduction band of ZnSe.

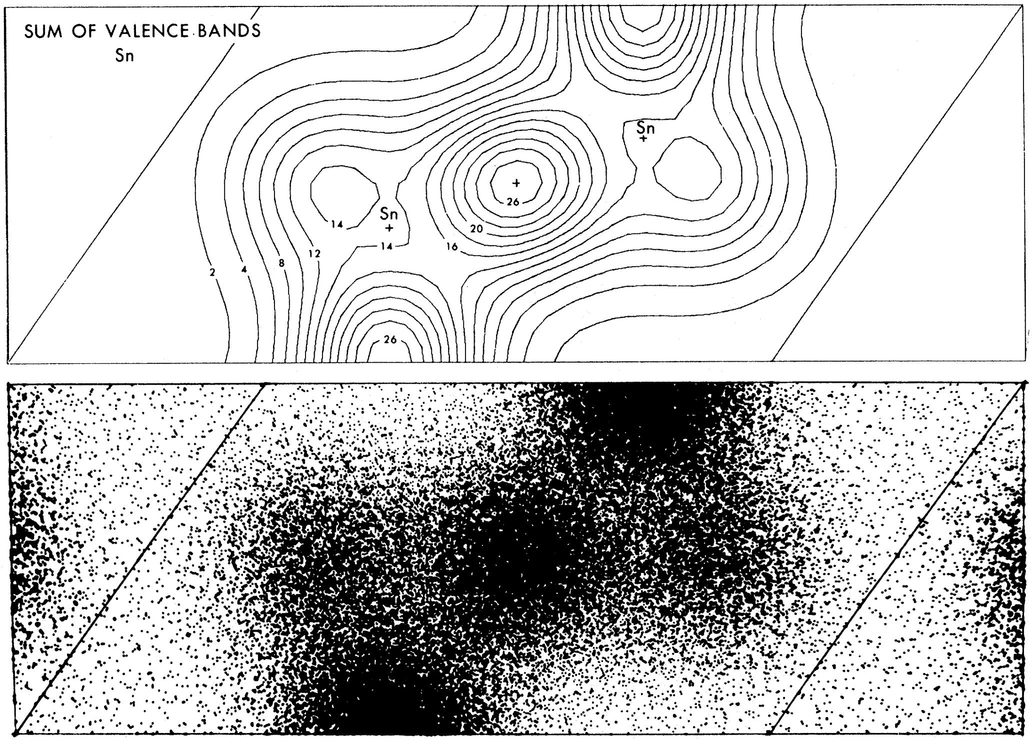

FIG. 20. Sn charge density for the sum of valence bands 1—4.

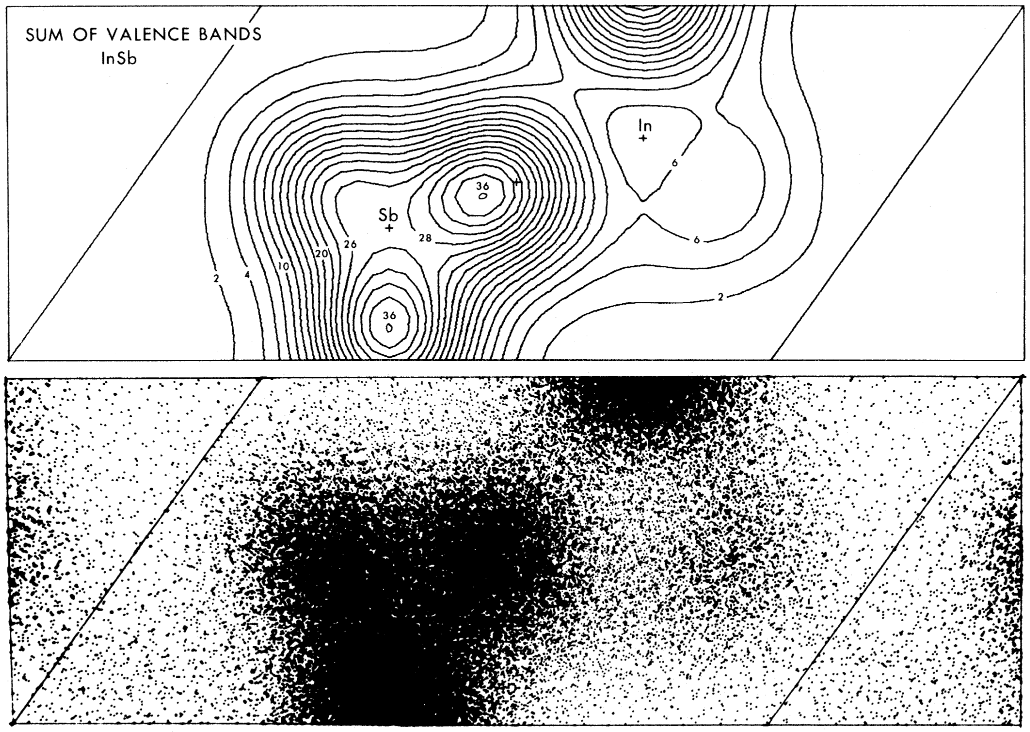

FIG. 21. InSb charge density for the sum of valence bands 1–4.

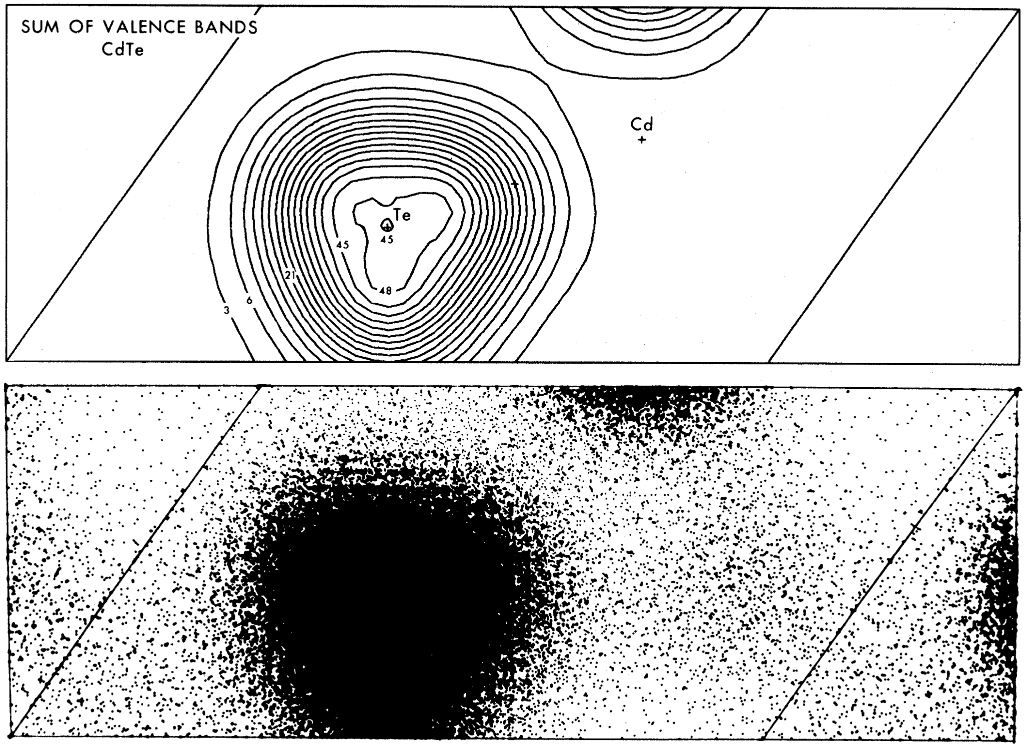

FIG. 22. CdTe charge density for the sum of valence bands 1–4.

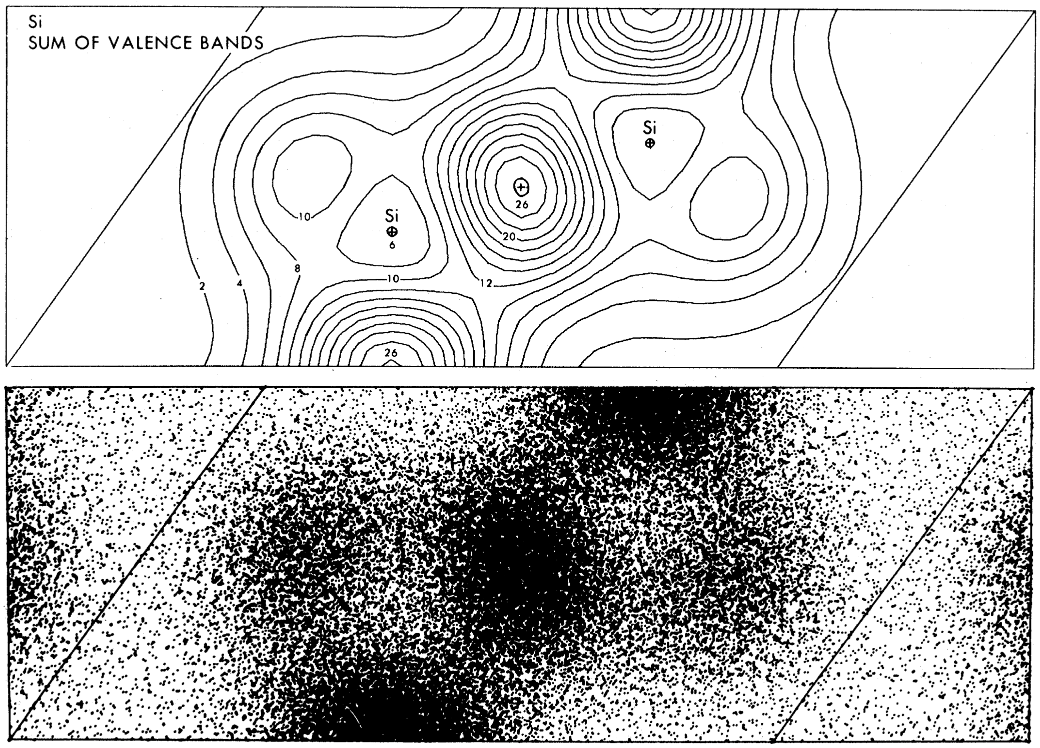

FIG. 23. Si charge density for the sum of valence bands 1–4. The core radii for Si are 0.16 of the Si–Si distance. The radii are those of spheres containing 80% of the outermost shell of core electrons.

and Sn, InSb, CdTe) we have discussed, the most noticeable trend is the piling of charge on the anion and a corresponding reduction of the covalent-bonding charge. Thus the covalent bonding becomes weaker as the crystals become more ionic.

The covalent-bonding charge Z_b may be calculated as follows:

$$Z_b = \sum_n \int (\rho_n(\vec{r}) - \rho_0)\, d^3r \;, \qquad (8)$$

where ρ_0 is the charge density at the outermost closed contour of the bonding charge density for each valence band.[13] The integration extends over the volume defined by this outermost contour; the integration was done numerically on a coarse grid. The values we calculate for Z_b (in units of e) are 0.146 for Ge, 0.080 for GaAs, 0.026 for ZnSe, 0.123 for Sn, 0.091 for InSb, and 0.027 for CdTe. Background problems are difficult and these results are only approximate.

Since the bonding charge Z_b is associated with the covalent properties of these crystals, it is interesting to compare these results with estimates of the covalency or ionicity of these crystals. We have compared our results with the ionicity scales of Phillips and Van Vechten and of Pauling. Phillips and Van Vechten[2,3] define ionicity f_i using homopolar, heteropolar, and average energy gaps E_h, C, and E_g, respectively, where $E_g^2 = E_h^2 + C^2$. Their ionicity factor $f = C^2/E_g^2$ varies between 0 and 1: $f_i = 0$ designates a completely covalent-bonded crystal and $f_i = 1$ designates a completely ionic crystal. An important result is that for Phillips's sample[3] of 68 binary crystals, the ionicity value $f_c = 0.785 \pm 0.01$ neatly separates the more covalent crystals of fourfold coordination (zinc-blende and wurtzite structures) from the more ionic crystals of sixfold coordination (rocksalt structure). As Phillips notes in his review article,[3] this critical value of the ionicity f_c is determined completely empirically.

We have attempted to obtain f_c from our calculation of bonding charge. The idea is that atoms in crystals of fourfold coordination form tetrahedrally directed covalent bonds through hybridization of [e.g., (sp^3) in Ge] orbitals, and that crystals of sixfold coordination no longer form directed bonds but are held together by electrostatic forces. For an homologous series of crystals of increasing ionicity, the covalent bonding weakens as the ionic bonding becomes stronger. When the amount of charge in the covalent bond approaches zero, the configuration of tetrahedrally directed bonds is no longer stable. Consequently, it is reasonable to speculate that a phase transition to a different crystalline structure occurs as the covalent-bonding charge is close to zero.

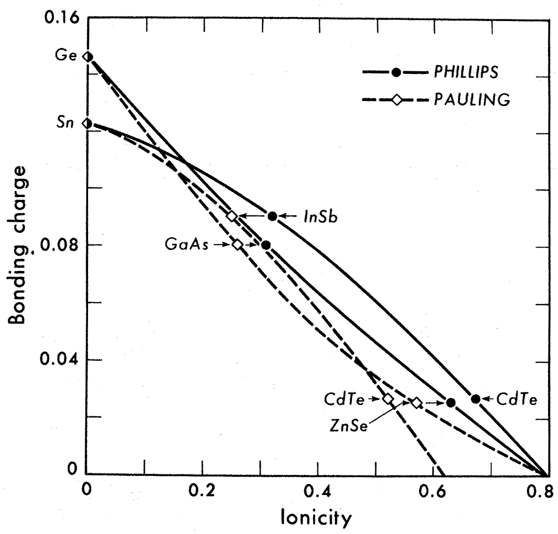

FIG. 24. Bonding charge vs ionicity. The bonding charge is in units of e per bond. The calculations do not include spin-orbit effects.

To test this hypothesis we have plotted in Fig. 24 our calculated values of Z_b vs the ionicity of Phillips and Van Vechten for the series of compounds studied. The points of the series Ge, GaAs, and ZnSe[14] are connected with a smooth curve, which when extrapolated gives zero bonding at an ionicity of $f_c = 0.78$. The points of the series Sn, InSb, and CdTe are also connected using a smooth curve, which when extrapolated gives zero bonding at an ionicity of $f_c = 0.79$. These two values of critical ionicity ($f_c = 0.79$ and $f_c = 0.78$) should be compared with Phillips's empirical value of the critical ionicity, namely, $f_c = 0.785 \pm 0.01$.

When the bonding charge Z_b is plotted (Fig. 24) against Pauling's ionicity scale,[15] the curve pass-through the series Ge, GaAs, and ZnSe gives a zero-covalent-bonding ionicity of 0.80, which is the value empirically determined by Phillips for the critical ionicity using Pauling's scale. The curve passing through the series Sn, InSb, and CdTe gives a critical ionicity of 0.61, which does not agree very well with the above value. We conclude, therefore, that for the crystals we have studied it appears that the ionicity scale of Phillips and Van Vechten is in better agreement with our results than the ionicity scale of Pauling.

The discussion above is based on the plot in Fig. 24 where we have drawn what we believe to be a suitable curve between the calculated points. A least-squares fit to the points might be even more appropriate.[16] An analysis of this type would give roughly the same f_c value given above with a wider range of uncertainty. We should also point out that the transition from a fourfold to sixfold coordination is expected to occur in a region *close to* the $Z_b = 0$ point and not necessarily at this point. Because of this and the background problems in calculating Z_b, we expect that our values of f_c are approximate. It is encouraging that the values were so close to those obtained empirically by Phillips.

ACKNOWLEDGMENTS

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[7] J. C. Phillips, *Covalent Bonding in Crystals, Molecules and Polymers* (Chicago U. P., Chicago, 1970).

[8] See M. L. Cohen and V. Heine, in *Solid State Physics*, Vol. 24, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), and references therein.

[9] The pseudopotential form factors are taken from the following papers: Si, Ge, and Sn: M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966); GaAs: R. R. L. Zucca, J. P. Walter, Y. R. Shen, and M. L. Cohen, Solid State Commun. 8, 627 (1970); ZnSe: J. P. Walter, M. L. Cohen, Y. Petroff, and M. Balkanski, Phys. Rev. B 1, 2661 (1970); InSb: R. Boyd, J. P. Walter, and M. L. Cohen (unpublished); CdTe: D. Chadi, J. P. Walter, and M. L. Cohen (unpublished).

[10] Since the wave functions are obtained using a pseudopotential (core states are not included), $\rho_n(r)$ is not expected to be accurate in the neighborhood of the ion core.

[11] The reader should note that only 20 to 25 plane waves are needed for convergence in the calculation of energy eigenvalues and of dipole matrix elements needed for detailed calculations of reflectivity spectra [see J. P. Walter and M. L. Cohen, Phys. Rev. 183, 763 (1969)]. This apparently small number of plane waves is sufficient because the effect of an additional 80 plane waves is incorporated by the use of a perturbation technique due to Löwdin [see P. O. Löwdin, J. Chem. Phys. 19, 1396 (1951)]. In the present calculation the Löwdin perturbation method is not used.

[12] A. Streitweiser, Jr., *Molecular Orbital Theory for Organic Chemists* (Wiley, New York, 1961).

[13] The chief difficulty is obtaining a measure of the bonding charge against a complicated background. The method used here is simple and physically reasonable. The bonding charge is evaluated for each band and then summed because it is easier to separate bonding charge from background of an individual band.

[14] The ionicity of ZnSe on Phillips's scale is 0.63 [J. C. Phillips (private communication)].

[15] L. Pauling, *The Nature of the Chemical Bond* (Cornell U.P., Ithaca, N. Y., 1939). The values of the ionicity for Pauling's scale are actually calculated by Phillips in Ref. 3.

[16] L. Pauling (private communication).